

Original paper

Ag, Cu, Hg, Pt, Sb and Te substitutions in the synthetic analogue of palladseite, Pd₁₇Se₁₅: an experimental mineralogical study

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The solubility of Ag, Cu, Hg, Pt, Sb and Te in the synthetic analogue of palladseite was experimentally studied at 350 °C. To document the impact of these elements on the palladseite crystal structure, Rietveld refinement analysis of experimental products was performed. The synthetic Pd₁₇Se₁₅ dissolves at 400 °C 3.6, 6.4, 8.8, 9.7, 6.1 wt. % of Cu, Ag, Hg, Pt and Te, respectively. The solubility of Sb in synthetic Pd₁₇Se₁₅ is less than 0.03 wt. %. Three different types of incorporation of the above-mentioned elements to the palladseite structure have been observed. Ag, Cu and Hg occupy a position 3d of the *Pm*–*3m* space group, which was empty in the unsubstituted Pd₁₇Se₁₅. Consequently, Pd occupancy of adjacent [Pd(4)Se₆] octahedron is reduced to 0.46 and 0.51 for Cu and Ag-bearing palladseite, respectively. Incorporation of Hg to the palladseite structure causes vacancy of this Pd(4) position. Pt partially substitutes Pd at the Pd(2) position (6f), forming Pd_{0.41}/Pt_{0.59} mix site showing square-planar coordination by Se atoms. Te atoms substitute for Se. The refined unit-cell parameter increased from the initial value of *a* = 10.6074(1) Å for Pd₁₇Se₁₅ to 10.6680(1) Å for Te-bearing palladseite. Incorporation of Cu, Ag and Hg to the palladseite causes significant changes of its powder X-ray diffraction pattern and hence can be detected by PXRD.

Keywords: palladseite, Pd₁₇Se₁₅, powder X-ray diffraction, Rietveld method, substitutions

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1. Introduction

Palladseite, Pd₁₇Se₁₅ was described as a new mineral by Davis et al. (1977) from residual concentrates from gold washing at Itabira, Minas Gerais, Brazil, where it is associated with arsenopalladinite, isomertieite and atheneite. Palladseite is known to occur in auriferous mineralization, also locally known as jacutinga type ores, in Minas Gerais and Serra Pelada in Brazil (Olivo and Gauthier 1995; Cabral et al. 2002; Cabral and Lehmann 2007). In Itabira, palladseite is the dominant selenide mineral, accompanied with chrisstanleyite (Ag₂Pd₃Se₄), a phase analogous to tischendorfite (Pd₈Hg₃Se₉), sudovikovite (PtSe₂) and phases with the empirical composition of Pd₅(Hg,Sb,Ag)₂Se₆ and (Pd,Sb,Ag,Hg)₅Se₄, respectively (Cabral and Lehmann 2007). Palladseite was also reported from gold-palladium mineralization at Bleida Far West, Bou Azzer–El Graara Inli er, Anti-Atlas in Morocco (El Ghorfi et al. 2006).

According to the study of Davis et al. (1977), palladseite is isostructural with a synthetic Pd₁₇Se₁₅ (Geller 1962). Palladseite has an ideal chemical composition of Pd₁₇Se₁₅, however, published electron microprobe analyses of palladseite often contain minor content of copper, silver, mercury and platinum as a non-essential constituent. Cabral et al. (2002) reported minor amounts of Pt (0.6–3.5 wt. %),

Cu (2.9–3.5 wt. %), Hg (0.9–1.9 wt. %) and Ag (0.3–0.5 wt. %) for palladseite from the Cauê iron-ore mine, Minas Gerais, Brazil. Cabral and Lehmann (2007) indicated 3.89 wt. % of Hg and 4.43 wt. % of Ag for palladseite-like mineral from Gongo Soco, Brazil. The original description of palladseite by Davis et al. (1977), reported chemical formulae of (Pd_{15.47}Cu_{1.85}Hg_{0.21})_{Σ17.56}Se_{14.43}, where copper and mercury were regarded as non-essential constituents. The experimental work of Ag–Pd–Se system of Vymazalová et al. (2014), revealed solubility of 7 wt. % of Ag in the synthetic analogue of palladseite at 350 °C. Drábek et al. (2014) carried out an experimental study of Pd–Hg–Se system and described 8.5 wt. % solubility of Hg in the synthetic analogue of palladseite at 350 °C. Makovicky and Karup-Møller (2017) reported significant Cu solubility in Pd₁₇Se₁₅ in their experimental study. Palladseite is stable up to 680 °C (Olsen et al. 1979).

In order to explain the incorporation of Ag, Cu, Hg and Pt and to define their maximal extent of solubility, an experimental study with the synthetic analogue of palladseite and third element was performed at 400 °C. Although Sb and Te are not reported to occur in significant amounts in palladseite, their potential solubility in synthetic palladseite was also experimentally studied. To document the impact of the elements mentioned above

on the palladseite crystal structure, Rietveld refinement analysis of the experimental products was performed.

2. Experimental procedures

2.1. Synthesis

Experiments were performed in evacuated and sealed silica glass tubes in horizontal tube furnaces in the Laboratory of Experimental Mineralogy at the Czech Geological Survey. To prevent a loss of material to the vapor phase during experiments, the free space in the tubes was reduced by placing closely fitting glass rods over the charge. Charges of about 300 mg were carefully weighed out from the native elements. We used, as starting chemicals, palladium powder (99.95% purity), selenium pebbles (99.999% purity), and silver powder (99.9999% purity), platinum powder (99.95% purity), copper ingot (99.999% purity), tellurium ingot (99.999% purity), and mercury (99.999%). The starting mixtures were first heated at 300 °C after melting at 1000 °C and then heated at 400 °C for two months. In order to attain the equilibrium, the run products were twice reground under acetone and reheated to the required temperature. After heating, quenching occurred by dropping the capsules in cold water. The starting compositions were weighted in the following ratio: 5Pd+4Se+1X, where X is Ag, Cu, Hg, Pt, Sb and Te.

2.2. Chemical composition of experimental products

Electron probe micro-analyses (EPMA) on grains of experimental products were obtained using a WDS (Oxford

Instruments NanoAnalyses, Hugh Wycombe, UK) installed on an SEM Mira 3GMU FEG (Tescan), with analytical conditions of 15 kV, 8.7 nA, and counting times 20 s (on peak position) and 10 s (on the background). The spectra were collected on PdL_α, SeL_α, AgL_β, CuK_α, PtM_α, SbL_α, TeL_α and HgM_α, using pure elements Pd, Ag, Cu, Pt and Bi₂Se₃, Sb₂Te₃ and HgS as standards. The results of EPMA analyses are summarized in Table 1. Within the sample, several different grains of palladseite (on average $n = 7$) were analyzed.

Two different approaches were used for the calculation of the chemical formulae of substituted palladseities from electron-microprobe data. Considering the nature of the substitution of Ag, Cu, Hg and Pt to the palladseite structure (i.e., occupation of the interstitial 3d site, no substitution/vacancies on the Se sites, see below), the calculation were based on the basis of 15 Se atoms. Calculations of the chemical formula of unsubstituted Pd₁₇Se₁₅ and Te-bearing palladseite were performed on the basis of 32 *apfu*.

2.3. Powder X-ray diffraction analysis

Powder X-ray diffraction data of experimental products were collected in Bragg–Brentano geometry on a Bruker D8 Advance diffractometer equipped with the LynxEye XE detector and CuK_α radiation. Data were collected in the range from 10° to 140° 2θ with a step size of 0.015° 2θ and 1.2 second counting time per step. Qualitative phase analysis of samples was performed using HighScore program 3.0c (PANalytical 2011) and PDF-2 2018 database. The subsequent Rietveld refinements and calculations of difference Fourier maps were carried out by Topas 5 (Bruker AXS, 2014). Vesta program (Momma and Izumi 2011) was employed for visualizing difference electron densities.

The structural model of Geller (1962) for Pd₁₇Se₁₅ was transformed to a standard-setting (½ ½ ½ shift) of the *Pm*–*3m* space group and subsequently used as an initial structure model in our Rietveld refinements. In general, the refinements involved refinement of scale factors, unit-cell parameters, fractional coordinates and isotropic size and isotropic strain parameters. Since all atoms in the palladseite structure are in different special positions with 0, 1 or 2 degrees of freedom, only six positional parameters were refined. The background was

Tab. 1 Electron microprobe data (wt. %) for synthetic analogue of palladseite (Pd₁₇Se₁₅) and for Cu, Ag, Hg, Pt, Te-bearing palladseities.

palladseite	Mean	Range	SD	Cu-palladseite	Mean	Range	SD
Pd	60.54	60.22–60.85	0.22	Pd	57.47	56.86–58.24	0.57
Se	38.99	38.91–39.08	0.05	Se	39.06	38.76–39.27	0.19
				Cu	3.61	3.52–3.78	0.11
Ag-palladseite	Mean	Range	SD	Hg-palladseite	Mean	Range	SD
Pd	55.70	55.70–56.53	0.41	Pd	54.04	53.68–54.30	0.26
Se	37.34	36.78–37.89	0.55	Se	37.02	36.93–37.16	0.10
Ag	6.35	6.17–6.35	0.18	Hg	8.83	8.65–9.02	0.15
Pt-palladseite	Mean	Range	SD	Te-palladseite	Mean	Range	SD
Pd	52.58	52.41–56.68	0.11	Pd	58.74	58.46–59.00	0.20
Se	37.24	39.97–37.40	0.19	Se	34.24	33.92–34.46	0.19
Pt	9.65	9.41–9.85	0.18	Te	6.11	5.94–6.50	0.23
Sb-palladseite	Mean	Range	SD				
Pd	60.93	60.48–61.50	0.37				
Se	39.34	39.01–39.66	0.23				
Sb	0.02	0.00–0.03	0.01				

SD – standard deviation

Tab. 2 Crystallographic data and Rietveld analysis for synthetic analogue of palladseite (Pd₁₇Se₁₅), Cu, Ag, Hg, Pt and Te-bearing synthetic palladseities.

	palladseite	Cu-palladseite	Ag-palladseite	Hg-palladseite	Pt-palladseite	Te-palladseite
Crystal data						
Unit-cell content (Z = 2)*	Pd _{17.00} Se _{15.00}	Cu _{1.50} Pd _{16.73} Se _{15.00}	Ag _{1.50} Pd _{16.76} Se _{15.00}	Hg _{1.50} Pd _{16.50} Se _{15.00}	Pt _{1.86} Pd _{15.23} Se _{15.00}	Pd _{17.09} Te _{1.48} Se _{13.42}
Unit-cell parameter (Å)	10.6074(1)	10.6317(1)	10.6773(1)	10.6587(1)	10.6264(1)	10.6680(1)
Unit-cell volume (Å ³)	1193.51(3)	1201.75(3)	1217.25(3)	1210.91(3)	1199.94(3)	1214.07(3)
Rietveld analysis						
No. of reflections	274	276	283	279	276	275
No. of structural parameters	8	9	9	9	8	8
No. of profile parameters	2	2	2	2	2	2
R _p	0.073	0.047	0.063	0.054	0.072	0.075
R _{wp}	0.110	0.061	0.081	0.071	0.093	0.098

*Derived from structure refinement except for Te-bearing palladseite. Unit-cell content for Te-bearing palladseite was derived from electron-microprobe analysis.

determined employing a Chebyshev polynomial function of the 7th order. The Rietveld refinement strategies depend on the incorporated element and are described below. A similar strategy was applied for Cu, Ag and Hg bearing palladseities and different for Pt and Te-bearing ones. In order to reduce possible correlations between occupancy and displacement parameters, the isotropic

displacement parameters for all atoms were kept fixed to $B_{iso} = 0.25 \text{ \AA}^2$. No significant amount of Sb enters the palladseite structure (see below) and hence palladseite present in this experimental run was refined as a pure Pd₁₇Se₁₅. The results of Rietveld refinements are summarized in Tables 2 and 3, respectively. Figure 1 presents selected Rietveld fits.

Tab 3. Positions and occupancy parameters for synthetic analogue of palladseite (Pd₁₇Se₁₅), Cu, Ag, Hg, Pt and Te-bearing synthetic palladseities.

Palladseite						Cu-palladseite					
Atom	WN	x	y	z	Occ.	Atom	WN	x	y	z	Occ.
Pd1	24m	0.14789(5)	0.14789(5)	0.34917(8)	1	Pd1	24m	0.14844(5)	0.14844(5)	0.34912(8)	1
Pd2	6f	0.2614(2)	½	½	1	Pd2	6f	0.2614(2)	½	½	1
Pd3	3c	0	½	½	1	Pd3	3c	0	½	½	1
Pd4	1a	0	0	0	1	Pd4	1a	0	0	0	0.45(1)
Se1	12i	0	0.33120(9)	0.33120(9)	1	Se1	12i	0	0.3317(1)	0.3317(1)	1
Se2	12j	½	0.2707(1)	0.2707(1)	1	Se2	12j	½	0.2713(1)	0.2713(1)	1
Se3	6e	0.2410(2)	0	0	1	Se3	6e	0.2374(2)	0	0	1
						Cu	3d	½	0	0	1
Ag-palladseite						Hg-palladseite					
Atom	WN	x	y	z	Occ.	Atom	WN	x	y	z	Occ.
Pd1	24m	0.15011(7)	0.15011(7)	0.3454(1)	1	Pd1	24m	0.14896(5)	0.14896(5)	0.34548(9)	1
Pd2	6f	0.2624(2)	½	½	1	Pd2	6f	0.2609(2)	½	½	1
Pd3	3c	0	½	½	1	Pd3	3c	0	½	½	1
Pd4	1a	0	0	0	0.51(1)	Pd4	1a	0	0	0	0.00(1)
Se1	12i	0	0.3301(1)	0.3301(1)	1	Se1	12i	0	0.3304(1)	0.3304(1)	1
Se2	12j	½	0.2710(1)	0.2710(1)	1	Se2	12j	½	0.2703(1)	0.2703(1)	1
Se3	6e	0.2348(3)	0	0	1	Se3	6e	0.2246(2)	0	0	1
Ag	3d	½	0	0	1	Hg	3d	½	0	0	1
Pt-palladseite						Te-palladseite					
Atom	WN	x	y	z	Occ.	Atom	WN	x	y	z	Occ.*
Pd1	24m	0.14783(8)	0.14783(8)	0.3484(1)	1	Pd1	24m	0.1478(4)	0.1478(4)	0.3486(6)	1
Pd/Pt2	6f	0.2580(2)	½	½	0.41/0.51(1)	Pd2	6f	0.261(1)	½	½	1
Pd3	3c	0	½	½	1	Pd3	3c	0	½	½	1
Pd4	1a	0	0	0	1	Pd4	1a	0	0	0	1
Se1	12i	0	0.3309(2)	0.3309(2)	1	Se/Te1	12i	0	0.3368(9)	0.3368(9)	90/10
Se2	12j	½	0.2700(2)	0.2700(2)	1	Se/Te2	12j	½	0.2713(8)	0.2713(8)	90/10
Se3	6e	0.2413(2)	0	0	1	Se/Te3	6e	0.235(2)	0	0	90/10
Pd5	3d	½	0	0	0.18(2)						

*Occupancy parameters for Se/Te positions were derived from electron-microprobe data; WN – Wyckoff notation

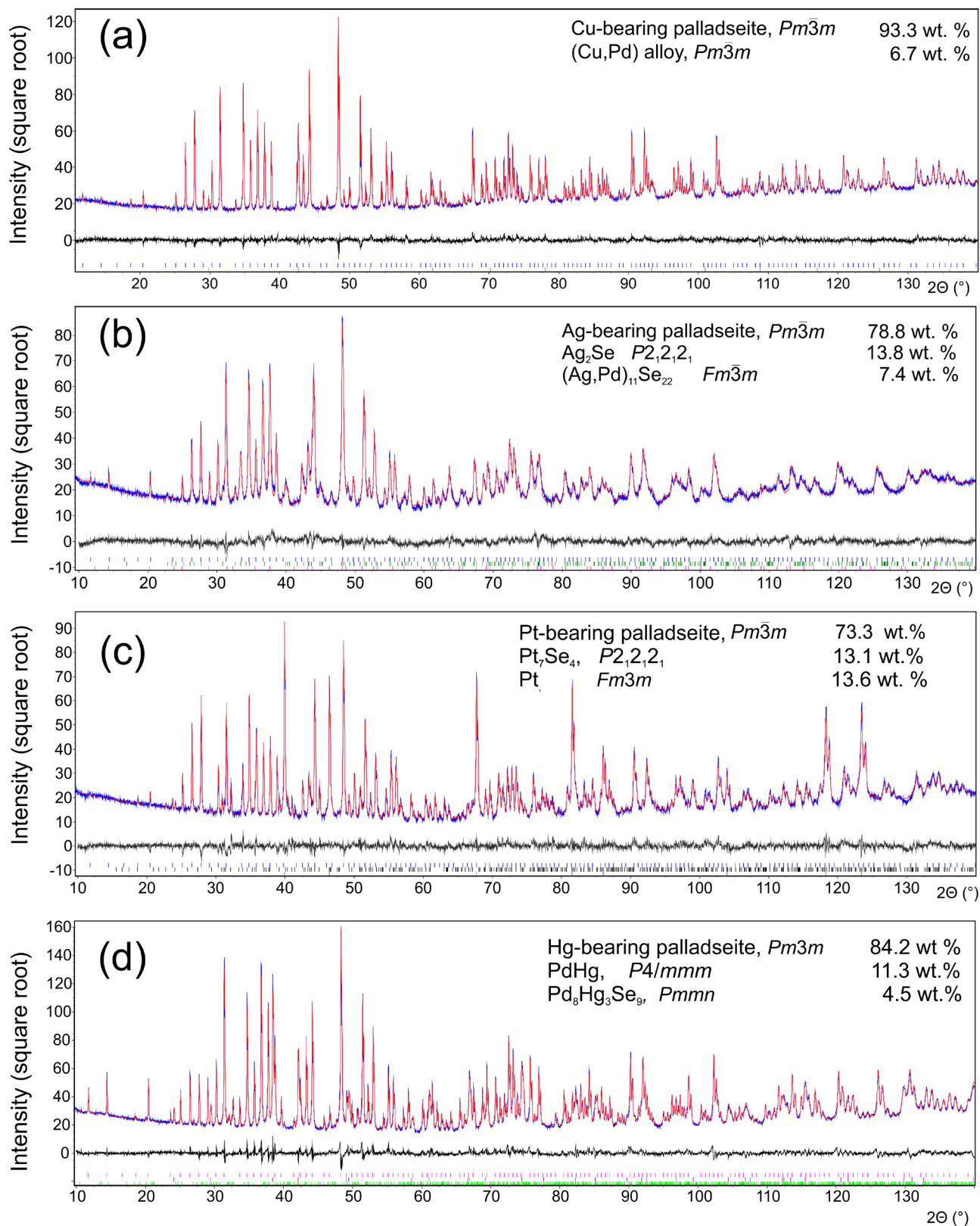


Fig. 1 Rietveld fits for (a) Cu, (b) Ag, (c) Pt and (d) Hg bearing palladseite.

2.3.1. Cu, Ag and Hg bearing palladseites

Initial Rietveld refinements of Cu, Ag and Hg-bearing palladseites using the structural model of Geller (1962) for Pd₁₇Se₁₅ yielded unsatisfactorily fits with of R_{wp} of 14.6, 19.6 and 30.74 %, respectively. An apparent mismatch was observed between the calculated and observed intensities of reflections (e.g., for 211, 311 and 311), especially for Hg-bearing palladseite. It is interesting to note that no additional reflections indicating a reduction of $Pm\text{--}3m$ symmetry and/or change of lattice were observed. The subsequent calculations of difference Fourier maps (using a structure model of Geller 1962 for Pd₁₇Se₁₅) revealed a strong maximum of 22.1, 31.9 and 73.0 e.Å⁻¹ in the close vicinity of (½ 0 0) position (i.e., 3*d* site) for Cu, Ag and Hg bearing palladseites, indicating that some atoms are missing in the structure model. Placing Cu, Ag and Hg at this special position (3*d*) considerably improved the Rietveld fits and R_{wp} dropped to 7.43, 8.13 and 17.66 % for Cu, Ag and Hg bearing palladseites, respectively. However, the difference Fourier maps from refinements of Cu, Ag and Hg bearing palladseites still showed remarkable peaks of -12.4, -9.44 and -30.2 e.Å⁻¹, respectively, located close to the (0 0 0) position (i.e., 1*a*). This position is fully occupied by Pd(4) atoms in the Pd₁₇Se₁₅ structure. Therefore, the occupancy of this Pd(4) site was refined and provided 0.46, 0.51 and 0 occupancy of Pd for Cu, Ag and Hg bearing palladseites. Subsequently, occupancy of all sites was refined (Cu/Ag/Hg vs. vacancy, Pd vs. vacancy, Se vs. vacancy). However only Pd(4) site showed a significant deviation from a fully occupied position. The final cycles of Rietveld refinements converged to 4.72, 8.13 and 7.12 % of R_{wp} for Cu, Ag and Hg bearing palladseites, respectively.

2.3.2. Pt bearing palladseite

Initial Rietveld refinement of Pt-bearing palladseite using the structural model of Geller (1962) for Pd₁₇Se₁₅ provides a fairly acceptable fit with R_{wp} of 11.86 %, which suggests a different way of Pt incorporation to the palladseite than in the case of Hg, Cu and Ag. Nevertheless, the difference Fourier map revealed a strong maximum of 17.3 e.Å⁻¹ located at the nearest vicinity of the Pd(2) site (6*f* position), indicating substitution of this site by a heavier element. Considering the chemical composition, this site was thought to be a Pt/Pd mixed position. The following refinement using the scattering curves of Pt vs. Pd gave the Pd_{0.41}Pt_{0.59} site population. Occupancy of other sites was also refined, however, none of them shows deviation from a fully occupied position. Next difference Fourier map showed a maximum of 13.6 e Å⁻¹ at the vicinity of 3*d* position, indicating a partially occupied position. With respect to the limitations of Rietveld

refinement and correlations between refined parameters, it is impossible to distinguish if this position is partly occupied by Pt instead of Pd. However, considering the strong coordination preference of Pt for square coordination (i.e. in Pt/Pd2 site), the 3*d* position is likely occupied by Pd. The final refinement yielded 0.18 occupancy of this position by Pd. The final cycles of Rietveld refinement converged to 9.32 % of R_{wp} .

2.3.3. Te bearing palladseite

Initial Rietveld analysis of Te-bearing palladseite using the model of Geller (1962) provided an acceptable fit with R_{wp} = 10.75 %. The position 3*d* was found empty and Pd(4) site was fully occupied by Pd. The chemical data from electron microprobe analysis gave Pd_{17.09}Te_{1.48}Se_{13.42} (based on 32 *apfu*) chemical formulae, which indicates Se for Te substitution. Hence, all Se sites were changed to be Se/Te mixed positions with occupancy parameters derived from electron-microprobe data (i.e., Se_{0.90}Te_{0.10}) and fixed during the refinement. The final cycles of Rietveld refinement converged to 9.75 % of R_{wp} .

3. Results and Discussion

3.1. Synthetic analogue of palladseite Pd₁₇Se₁₅

The crystal structure of synthetic Pd₁₇Se₁₅ was solved by Geller (1962). Our Rietveld refinement has confirmed the structure model of Geller (1962) for synthetic Pd₁₇Se₁₅ and converged to the satisfactory profile agreement factors of R_{wp} = 9.29 % and R_p = 7.36 %. A detailed description of this structure type was also given by Dubost et al. (2007) for an isostructural synthetic phase Ni_{9.54}Pd_{7.46}S₁₅. Since the description of the palladseite structure is important in the following consideration, it is briefly discussed here. The interatomic distances discussed in this paragraph are based on our Rietveld refinement of synthetic Pd₁₇Se₁₅.

The crystal structure of palladseite is depicted in Fig. 2a and contains four Pd and three Se independent positions, all of them are in special positions with 0, 1 or 2 degrees of freedom for positional parameters. The coordination geometry of the Pd(1) site can be viewed as a transition between tetrahedral and square planar. It can be described as a strongly deformed tetrahedron flattened on one of its four axes with Pd–Se distances ranging from 2.44(1) to 2.505(8) Å. Pd(2) and Pd(3) sites form a nearly regular square with Pd–Se distances of 2.433(1) Å and 2.532(1) Å, respectively. Pd(3) position also has two short contacts at distances of 2.773(2) Å with adjacent Pd(2) positions, whereas Pd(2) site shows only

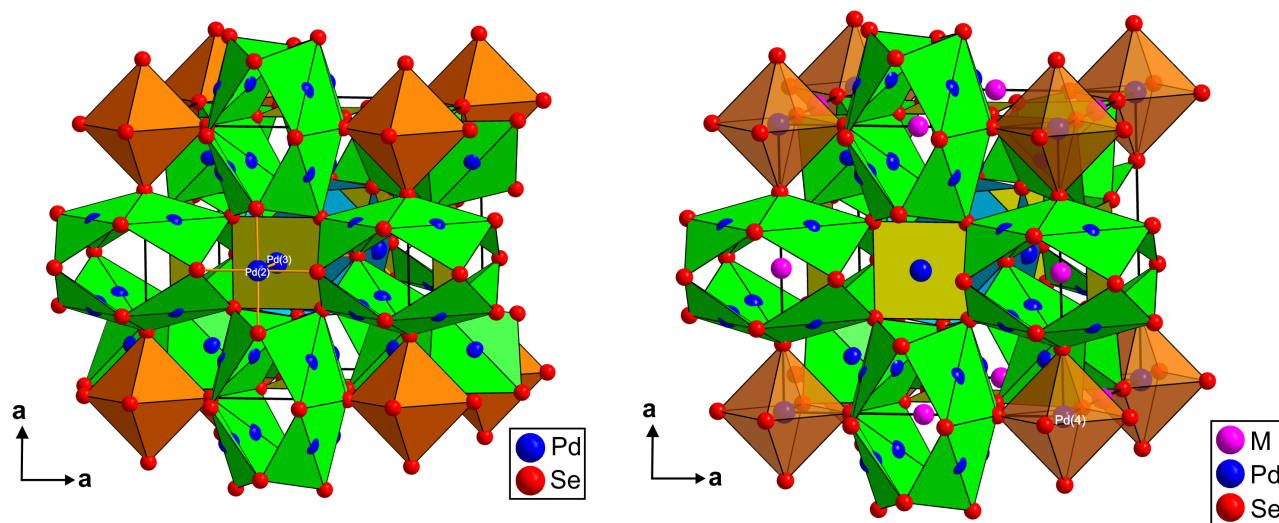


Fig 2. Polyhedral representation of (a) palladseite and (b) M -bearing palladseite ($M = \text{Cu}, \text{Ag}$ or Hg). Note the empty $3d$ position for $\text{Pd}_{17}\text{Se}_{15}$. The $[\text{Pd}(4)\text{Se}_6]$ octahedra are partly occupied in Ag and Cu -bearing palladseite and vacant in Hg -bearing palladseite.

one contact with Pd(3) position. According to Dubost et al. (2007), the metal-metal interactions might explain slightly longer Pd(3)–Se distances, 2.532(1) Å, than are the common values for Pd in square coordination by Se. Pd(4) atom is surrounded by six Se atoms at distance of 2.556 Å forming a regular octahedron.

It is interesting to note that already Geller (1962) mentioned in his original structural description of $\text{Pd}_{17}\text{Se}_{15}$ structure, presence of apparently large vacancies in the $3c$ position (i.e., $3d$ position after standardization) at $(\frac{1}{2} 0 0)$ of the $Pm\text{-}3m$ space group. This vacant position is surrounded by eight Pd(1) atoms forming a cube and two Se(3) atoms at distances of 2.735(1) Å and 2.747(3) Å, respectively. As is shown in Fig. 2b, this vacant space in the structure is defined by a group of eight $[\text{Pd}(1)\text{Se}_4]$ flattened tetrahedra forming a scallop-like polyhedron.

Geller (1962) pointed out that it would appear possible that some atoms would enter this site. As is shown below, this Geller (1962) observation was in principle correct since this position plays a fundamental role in the accommodation of Cu, Ag and Hg in the palladseite structure.

In accord with the refinement of Geller (1962), the position $3d$ was found empty during our Rietveld refinement. No significant residuals of electron densities were found at this position in difference Fourier maps in the structure of synthetic $\text{Pd}_{17}\text{Se}_{15}$. The occupancy parameters of all positions were allowed to vary (Pd vs. vacancy, Se vs. vacancy). All sites were found to be consistent with a pure occupation by Pd or Se, respectively, yielding $\text{Pd}_{17.00}\text{Se}_{15.00}$ structural formulae ($Z = 2$). This is consistent with a chemical composition of $\text{Pd}_{17.12}\text{Se}_{14.87}$ obtained from electron microprobe analysis.

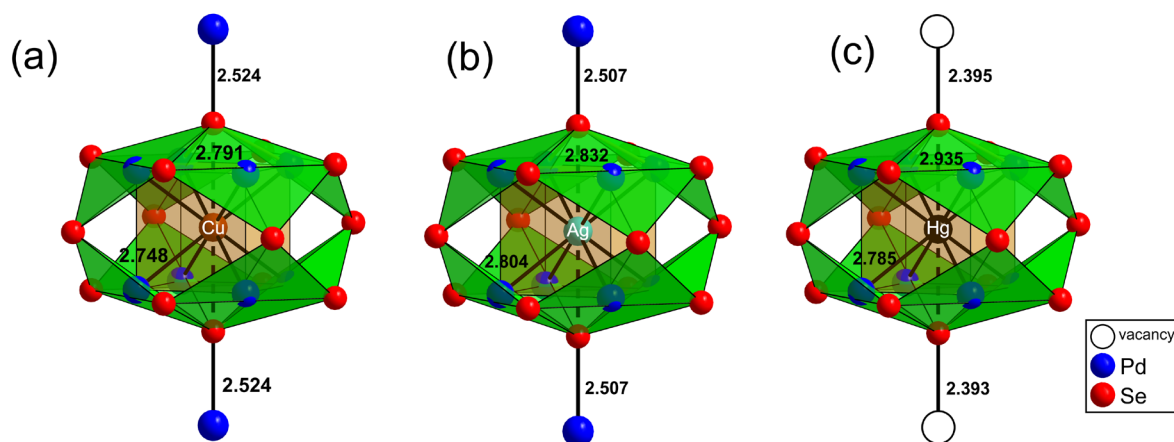


Fig 3. Detailed view of the coordination of Cu, Ag and Hg occupying the $3d$ position in the Ag, Cu, Hg-bearing palladseities.

3.2. Position of Cu in the palladseite Pd₁₇Se₁₅ structure

According to electron microprobe analysis, synthetic analogue of palladseite Pd₁₇Se₁₅ dissolves at 400 °C 3.61 wt. % of Cu. The formula obtained from the structural refinement yielded Cu_{1.50}Pd_{16.73}Se_{15.00}, which is in line with that obtained from electron microprobe data Cu_{1.72}Pd_{16.38}Se_{15.00}. Cu occupies the position 3*d* of the *Pm*-3*m* space group, which is empty in Pd₁₇Se₁₅ crystal structure. The crystal structure of Cu-bearing palladseite is depicted in Fig. 2b. Cu is surrounded by eight Pd(1) atoms at 2.748 (1) Å, forming cubic coordination and showing two additional short contacts with Se(3) atoms at 2.791(1) Å (Fig. 3). These Cu–Pd and Cu–Se distances are slightly longer (0.01 and 0.05 Å) than corresponding separations from the vacant 3*d* site in the Pd₁₇Se₁₅ structure. In contrast, the Pd(4)–Se distances (2.524(1) Å) in a partially occupied [Pd(4)Se₆] octahedra are about 0.02 Å shorter than those in full occupied [Pd(4)Se₆] octahedron in the pure Pd₁₇Se₁₅. The sum of these the Pd(4)–Se and Cu–Se bonds results in the increased value of the unit-cell parameter $a = 10.6317(1)$ Å in comparison with its unsubstituted analog, Pd₁₇Se₁₅, $a = 10.6074(1)$ Å.

3.3. Position of Ag in the palladseite Pd₁₇Se₁₅ structure

The structure derived a formula for Ag-bearing palladseite is Ag_{1.50}Pd_{16.76}Se_{15.00}, electron microprobe analysis yielded Ag_{1.86}Pd_{16.72}Se_{15.00} formula. Considering that Ag and Pd are neighbours in the periodic system and show very similar scattering curves for X-ray, the current Rietveld analysis does not provide any direct information about the degree of ordering/distribution between Ag and Pd atoms. The possibility that a certain degree of mixing of the Ag and Pd atoms occurs cannot be ruled out. By analogy to Cu, Ag occupies the 3*d* position in the palladseite structure. In the structure of Ag-bearing palladseite, Ag is surrounded by eight Pd(1) atoms at a distance of 2.804 Å and two Se(3) atoms at 2.832 Å (Fig 3). The Pd(4)–Se distances in partly occupied [Pd(4)Se₆] octahedron are 2.507 Å. These distances result in the unit-cell parameter $a = 10.6773$ Å for Ag-bearing palladseite.

3.4. Position of Hg in the palladseite Pd₁₇Se₁₅ structure

Structure derived formula of Hg-bearing palladseite is Hg_{1.50}Pd_{16.50}Se_{15.00} ($Z = 2$). It is in good agreement with EMPA data, which yields Hg_{1.41}Pd_{16.25}Se_{15.00} formulae. Hg occupies the 3*d* position in the palladseite structure. Incorporation of a large atom as Hg to the palladseite structure causes slight reorganization of the palladseite

structure. Hg show eight Pd(1) and two Se contacts at 2.785 and 2.935 Å, respectively. Hg–Se bonds are parallel to the [100] direction, together with Pd(4)–Se bonds. The Hg–Se distance is 0.19 Å larger than the corresponding distance observed in unsubstituted Pd₁₇Se₁₅. This, in turn, causes a reduction of Pd(4)–Se distance to the value of 2.395 Å, which is too short [Pd(4)Se₆] fully occupied octahedron. Consequently, the presence of large Hg atoms and subsequent long Hg–Se bonds might be a reason for a vacant Pd(4) site in the Hg-bearing palladseite. Hg-bearing palladseite shows a slightly larger value of the unit-cell parameter of 10.6587 Å than the unsubstituted Pd₁₇Se₁₅. However, even this expansion of the unit-cell cannot provide enough space and compensate for the increase of Hg–Se bonds in the scallop-like polyhedra and hence Pd(4) site (i.e., 1*a* position) is vacant. The Se–Se separation in the edge of this Se-based octahedron is 3.385 Å, which is 0.23 Å shorter than the corresponding value for unsubstituted Pd₁₇Se₁₅. Similar values of Se–Se separations were reported for shared edges of Se-based octahedra in tischendorfite (3.385 Å) and Pd₂HgSe₃ synthetic phase (3.419 Å) by Laufek et al. (2014, 2017), respectively. This distance is also considered as non-bonding since it is too far from a distance of ca. 2.35 Å common for Se–Se pairs (Jobic et al. 1990) in phases containing characteristic Se₂ dumbbells.

It is interesting to note that Hg-bearing palladseite has been relatively often reported in the literature (see Introduction) and even Hg was considered as a non-essential constituent in the original palladseite description as a new mineral by Davis et al. (1977). Consequently, such structural arrangement of Hg-bearing palladseities with no central cation (or with significant reduction of its occupancy) at 1*a* position seems to be a stable structural motive.

3.5. Position of Pt in the palladseite Pd₁₇Se₁₅ structure

Synthetic Pd₁₇Se₁₅ dissolves up to 9.65 wt. % Pt. The chemical formula derived from structure refinement of Pt-bearing palladseite is Pt_{1.86}Pd_{15.23}Se_{15.00} which agrees well with that obtained from electron microprobe Pt_{1.58}Pd_{15.71}Se_{15.00}. Pt partly substitutes Pd at the Pd2 position forming Pd_{0.41}Pt_{0.59} mixed site (6*f* position). This site is surrounded by four Se atoms showing nearly a square-planar coordination with Pd/Pt–Se bond distances of 2.446(1) and 2.447(1) Å. This is in line with the coordination preference of Pt²⁺ in chalcogenides with the $M:X$ ratio ($X = S, Se$ and Te) equal or smaller than one, where the Pt²⁺ assumes [Xe] 4*f*¹⁴ 5*d*⁸ electronic configuration and exhibits spin-paired square-planar coordination.

The partial Pt–Pd substitution does not significantly impact the *metal*–Se bond lengths, since these values are

practically identical to those of pure Pd₁₇Se₁₅. It is interesting to note, that Pt substitutes Pd only at the Pd(2) site. No Pt–Pd substitution on Pd(3) site, which also forms [PdSe₄] square, was observed. The reason for this might be related to a different number of *metal–metal* contacts for Pd(2) and Pd(3) sites; i.e., one and two *metal–metal* contacts for Pd(2) and Pd(3) sites, respectively.

3.6. Position of Te in the palladseite Pd₁₇Se₁₅ structure

According to electron microprobe analysis, synthetic palladseite dissolves up to 6.11 wt. % of Te. The chemical formula derived from EMPA is Pd_{17.09}Te_{1.48}Se_{13.42} (based on 32 *apfu*), indicating Se for Te substitution. The refinement revealed increased value of the unit-cell parameter, $a = 10.6677(1)$ Å, in comparison to pure Pd₁₇Se₁₅, $a = 10.6074(1)$ Å. This can be explained by larger atomic radii of Te (1.36 Å) with respect to the smaller radii of Se (1.17 Å) (Emsley 1989).

3.7. Incorporation of Sb in the palladseite Pd₁₇Se₁₅ structure

The experimental product of heating of Pd₁₇Se₁₅ with Sb in silica glass tube consists of Pd₁₇Se₁₅, Pd₇Se₄ and a new ternary phase Pd₁₁Sb₂Se₂. According to the electron microprobe analysis, the Sb content in Pd₁₇Se₁₅ is less than 0.03 wt. %. Sb does not enter the palladseite structure significantly and forms a separate phase Pd₁₁Sb₂Se₂. Its crystallographic characterization will be the subject of a separate paper.

3.8. Effect of Ag, Cu, Hg, Pt and Te substitution on the bond lengths in the palladseite crystal structure

Table 4 presents selected bond-lengths in the synthetic palladseities in the current study. As is evident from this table, the substitution of (Ag,Cu), and Hg influences mainly the Pd–Se bonds in the [Pd(4)Se₆] octahedra, which is adjacent to the scallop-like polyhedra contain-

ing the entering metal. As the *metal–Se* separations in the scallop-like polyhedra increase (from 2.747 Å for vacant-Pd₁₇Se₁₅ to 2.935 Å for Hg-palladseite), the Pd(4)–Se distances significantly reduce (from 2.556 to 2.395 Å for vacant and Hg-bearing palladseities, respectively). This reduction of Pd(4)–Se distance cause partial occupancy of this Pd(4) site for Ag and Cu-bearing palladseities and Pd(4) vacant position for Hg-bearing palladseite. The unit-cell parameter is increasing during these substitutions (Table 2), however, even such expansion cannot compensate for the shortening of the corresponding Pd(4)–Se bonds and subsequent occupancy reduction for Pd(4) site. Incorporation of Te to the palladseite structure causes a slight increase of Pd–Se/Te bonds. It is interesting to note that the substitution of Ag, Cu, Hg, Pt and Te has only a slight effect on the Pd–Pd bonds in the palladseite structure.

4. Conclusions

Ag, Cu, Hg, Pt are common elements in the palladseite structure and are regarded as non-essential elements for palladseite. Three ways of substitution mechanism were revealed to occur in the palladseite structure and can be summarized as follows:

(i) Cu, Ag and Hg enter the palladseite structure in a significant amount (3.6, 6.4 and 8.8 wt. %, respectively) at 400 °C and occupy a position *3d* of the *Pm–3m* space group, which is empty in the unsubstituted Pd₁₇Se₁₅. Consequently, Pd occupancy of adjacent [Pd(4)Se₆] octahedron is reduced to 0.46 and 0.51 for Cu and Ag-bearing palladseite, respectively. Incorporation of Hg to the palladseite structure causes vacancy of this Pd(4) position. Incorporation of Cu, Ag and Hg to the palladseite causes significant changes of its powder X-ray diffraction pattern and hence can be detected by PXRD.

(ii) Synthetic Pd₁₇Se₁₅ dissolves up to 9.7 wt. % Pt at 400 °C. It is in agreement with the strong coordination preference of Pt⁺² with the [Xe] 4f¹⁴ 5d⁸ electronic configuration to form a square-planar arrangement. Pt atoms occupy the Pd(2) site with square-planar coordination by Se atoms.

Tab 4 Selected bond distances (Å) for synthetic analogue of palladseite (Pd₁₇Se₁₅), Cu, Ag, Hg, Pt and Te-bearing synthetic palladseities.

Sample	Occ. Pd(4)	M–Pd(1)*	M–Se	Pd(4)–Se	Pd(1)–Se	Pd(1)–Pd(1)**	Pd(3)–Pd(2)
palladseite	1	8×2.735	2×2.747	6×2.556	2.440 + 2.497 + 2×2.505	2×3.138 + 3.199	2×2.774
Cu-palladseite	0.46(1)	8×2.748	2×2.791	6×2.524	2.448 + 2.154 + 2×2.527	2×3.155 + 3.208	2×2.779
Ag-palladseite	0.51(1)	8×2.804	2×2.832	6×2.507	2.463 + 2.507 + 2×2.555	2×3.205 + 3.301	2×2.802
Hg-palladseite	0	8×2.785	2×2.935	6×2.395	2.461 + 2.507 + 2×2.589	2×3.176 + 3.294	2×2.781
Pt-palladseite	1	8×2.744	2×2.762	6×2.551	2.443 + 2.495 + 2×2.507	2×3.141 + 3.222	2×2.742
Te-palladseite	1	8×2.754	2×2.827	6×2.507	2.466 + 2.538 + 2×2.563	2×3.153 + 3.230	2×2.786

*M = Ag, Cu, Hg at *3d* site ($\frac{1}{2}$ 0 0) of the *Pm–3m* space group. This position is vacant in the palladseite and Te-palladseite and the distances presented here represent separation of empty *3d* position and surrounding Pd(1) and Se atoms.

** Represent Pd(1)–Pd(1) distances in the scallop-like polyhedra containing M in its center.

(iii) Te atoms enter the palladseite structure up to 6.1 wt. % at 400 °C and substitute for Se. The refined unit-cell parameter increased from the initial value of $a = 10.6074(1)$ Å for Pd₁₇Se₁₅ to 10.6680(1) Å for Te-bearing palladseite. No occupation of 3*d* interstitial site occurs.

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